

The thermal conductivities of mixtures of rare gases at 29°C and at 520°C

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With 6 figures in the text

ABSTRACT

The present investigation was aimed principally at the triple mixtures of He-Kr-Xe, which may occur in fuel elements of certain atomic reactors. However, because heat conductivities of mixtures of rare gases and conductivities at elevated temperatures altogether have been very little investigated, it was decided to extend the programme by including all the binary mixtures between the common rare gases He, Ne, Ar, Kr, and Xe and to measure at 29°C and at 520°C.

The method

Speed and ease of operation of the apparatus, perhaps with some sacrifice of absolute accuracy, was deemed paramount in order to collect the body of data aimed at. The hot-wire or Schleiermacher's method offered itself most advantageously, and the writer could further draw benefit from his previous experience with it (von Ubisch, 1951).

Referring for a more detailed discussion to the paper cited, the method may be described briefly as follows: A thin wire of exactly known diameter with high temperature coefficient of electrical conductivity is stretched coaxially within a tube of known diameter. The walls of the tube are kept at a fixed temperature. The wire forms part of a bridge circuit outlined in Fig. 1, which enables the energy dissipation of the wire at any specified temperature to be measured.

If the current through the wire is very low, and the generation of Joule's heat in the wire can be neglected, the setting of the precision resistance at the balance point (Fig. 1) gives the resistance of the wire at the temperature of the tube. For a measurement of heat conduction, the setting of the resistance is increased by a certain amount corresponding to desired increase of wire temperature. Next the current through the bridge is increased until the bridge balances once more. Then the vernier potentiometer which gives the current, is read and the heat generation is calculated from the data now available. The battery and rheostat at the lower right in the figure counterbalance thermoelectric forces from the high-temperature cell, if used.

The figure found for the heat dissipation is to be corrected for terminal losses, heat radiation, convective heat transfer in the gas and for a pressure effect

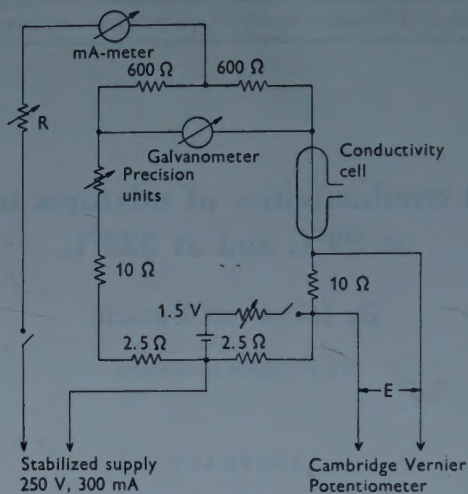


Fig. 1. Electrical circuit of conductivity apparatus.

which is a mean free path phenomenon called the "temperature jump". Terminal effects can be calculated, the radiation loss determined by a measurement in vacuo, and any pressure effects are dealt with by plotting the inverse values for the heat transfer through the gas versus the inverse pressure on a linear scale. Straight lines should result if convection is absent.

The graphical method results in a value of heat transfer extrapolated to zero mean free path or "infinite pressure" (i.e. $1/p = 0$). This value is inserted into the well-known formula for the heat transfer between cylinders

$$q = \frac{2\pi K \theta}{\ln r_2/r_1},$$

where q is the (corrected) heat dissipation of the wire per unit length, K is the thermal conductivity of the gas examined, and θ is the temperature difference between wire and tube and r_1 and r_2 are their respective radii. As far as the writer's experience goes, this method applies well to mixtures too, though no theory exists on their temperature jumps.

Apparatus

Two cells were used which were attached to a common vacuum system and alternately connected into the circuit of Fig. 1. One cell consisted of a pyrex tube, I.D. 20 mm, immersed in water at 25°C, the other was of stainless steel, I.D. 21 mm, surrounded with a jacket filled with molten tin at 500°C, and placed into a tubular furnace. In both cells tungsten wires with diameter 0.018 mm as determined by weight and with an apparently gray surface were used. Their lengths were 422 and 335 mm respectively. The wires were supported in one

case by a frame of two rods, in the other of 4 rods of diameter 1 mm. These frames were attached to a glass seal on top of the pyre tube, or to a demountable flange (aluminium gaskets) at the lower end of the steel tube, which protruded into the cold region below the furnace. This slight deviation from perfect circular geometry, due to the supporting frame, matters very little because of the logarithmic term in the formula for the heat conduction.

The temperature of the water was controlled by means of a mercury-filled contact thermometer, that of the tin by means of a laboratory-made resistance thermometer. Temperatures were measured by means of mercury thermometers and also a chromel-alumel thermocouple.

The writer preferred tungsten wires to platinum (von Ubisch, 1951). In the present apparatus they twice withstood an accidental inrush of air at 500°C with only a barely detectable change in resistance. The thin and long wires used have the advantage of establishing a temperature equilibrium very quickly. Further, any end effects are largely diminished, convection and thermomolecular currents are not likely to start (von Ubisch, 1952), and the heating currents are kept in the mA-range which is most easily handled by the today more common electronic equipment. The temperature jump effect is, however, enhanced for thin wires.

Procedure

Temperature differences between the wires and tubes were kept at 8° and 40° respectively. The two tubes behaved identically at room temperature. The heating currents at room temperature were 1.56 mA in vacuo and about 14 mA in xenon, and in the latter case the corrections for radiation and terminal losses together amounted to about 4 %. At 500°C the values were respectively 9.8 mA, 27 mA and 16 %. Pressures were kept in the case of Xe on the region 20–100 mm Hg, in He between 70 and 740 mm Hg, as measured in the cold part of the system. The jump effect was vastly more pronounced at the higher temperatures. Convection could not be detected in any case. About four or five measurements at different pressures were taken for each gas or mixture, using the same bridge circuit for both cells. The ternary mixtures of He with Kr and Xe have been made by gradually diluting with He the binary mixtures previously made up of Kr and Xe.

Gas samples

The helium was taken from a steel cylinder delivered by the Matheson Co., East Rutherford, N. J., the argon from AGA Gasaccumulator, Stockholm-Lidingö (a very pure gas used for welding), and the neon, krypton and xenon was "spectroscopically pure", delivered by Norsk Hydro, Rjukan, Norway.

Results

Table 1 lists the thermal conductivities of the pure gases. The reference temperature is the average of the wire and wall temperatures. The quantity s is a coefficient calculated from the relation

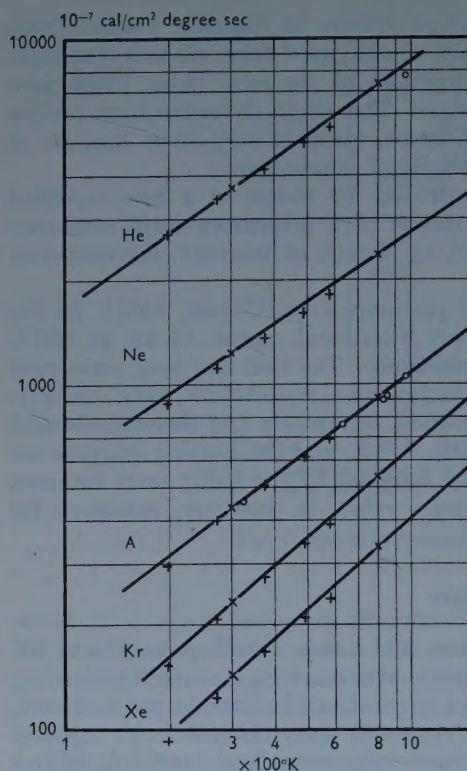


Fig. 2. Thermal conductivity of pure gases vs. temperature. $\times$, this investigation; $+$, Kannu-luik and Carman, 1952; O , Rothman, 1954.

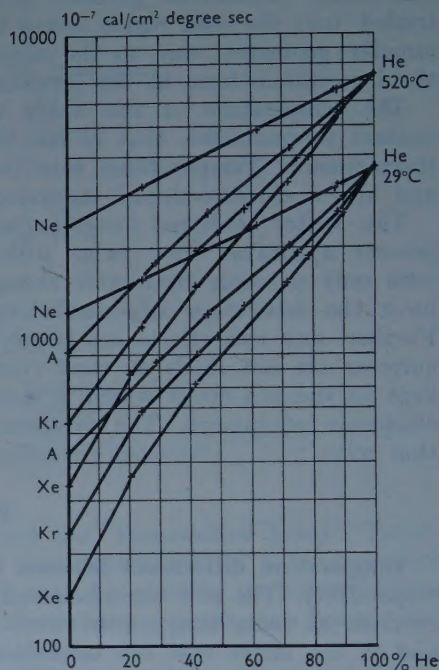


Fig. 3. Thermal conductivities of the binary mixtures of He with Ne, A, Kr and Xe.

Table 1. Thermal conductivities of pure gases (in units of 10^{-7} cal/cm² degree sec).

Gas	29°C	520°C	s
He	3670	7360	0.72
Ne	1237	2360	0.67
A	434	914	0.77
Kr	232	534	0.86
Xe	142.7	334	0.88

K prop. to T^s ,

where T is the Kelvin temperature.

Fig. 2 illustrates the temperature dependence for the pure gases on a log/log scale, which should result in straight lines if s is constant.

The thermal conductivities of all the binary mixtures are plotted in Figs. 3 to 5. Instead of the usual linear scale a semi-logarithmic scale has been used, which more clearly reveals a significant trend to be discussed below.

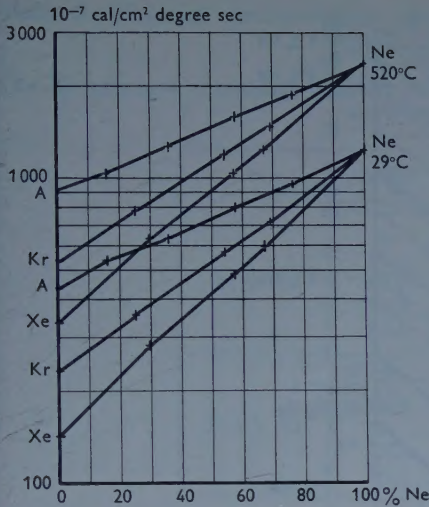


Fig. 4. Thermal conductivities of the binary mixtures of Ne with A, Kr and Xe.

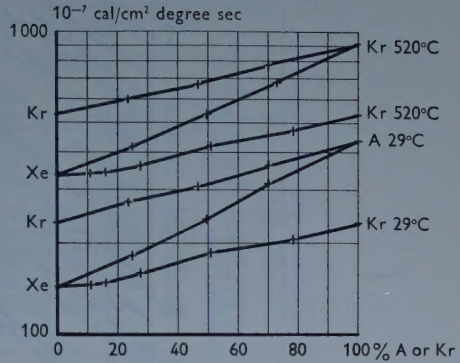


Fig. 5. Thermal conductivities of the binary mixtures of A with Kr and Xe and of Kr with Xe.

Graphs similar to Figs. 3 to 5 have been omitted for the ternary system of He-Kr-Xe. It was found that the curves were approximately evenly distributed between the curves for Kr-He and Xe-He in Fig. 3. The ternary system is accordingly described in Table 2. Of special interest for atomic energy purposes is the mixture which contains Kr and Xe in the ratio as stable and long-lived fission products. For the fission of U-235 this ratio is 15.3 atom % Kr and 84.7 atom % Xe, with atomic weights slightly above those of the atmospheric gases. A mixture which has approximately this composition has therefore been dealt with more extensively in Fig. 6. Due to the difference in isotopic composition its heat conductivity should be about 1.6 % better than that of the true fission product gas.

The precision of all the data obtained here is about $\pm 2\%$, as judged from repeated measurements on the same gases or mixtures. There is a further systematic difference of about 4 % if the present results are compared with those from other authors. This is seen clearly in Fig. 2. Most authors have preferred thick wires in their apparatus and therefore have large corrections for terminal losses and small ones for the temperature jump, whereas the opposite has been the case here. The systematic difference thus arising cannot properly be accounted for at the moment.

Discussion and comparisons with other results

Fig. 2, which deals with the temperature dependence, also contains values measured by Kannuliik and Carman (1952) and by Rothman (1954). Apart from the systematic deviation mentioned already, the dependence upon temperature is the same, and the exponential s in the equation given above appears to be reasonably constant in the region under investigation.

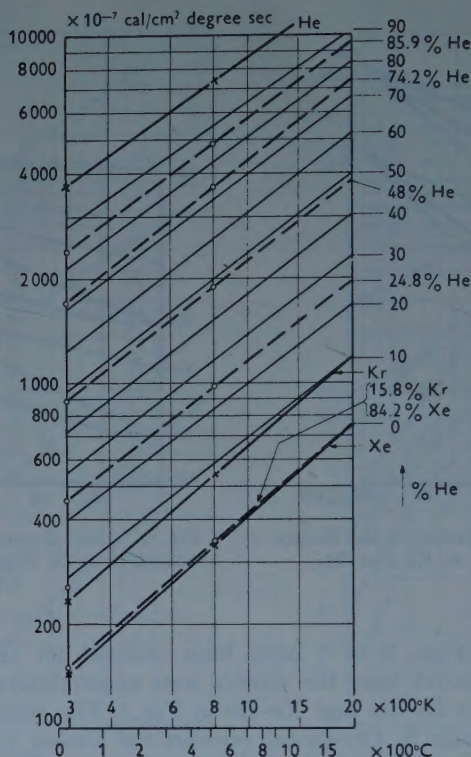


Fig. 6. Thermal conductivities of the ternary mixtures of He, Kr and Xe, where the ratio Kr/Xe is 15.8/84.2. The temperature is plotted along the abscissa.

The thermal conductivity of a binary mixture of gases is usually lower than the arithmetic mean calculated from the conductivities of the pure constituents. This means that in graphs similar to Figs. 3 and 5 but with a linear scale, the curves giving the thermal conductivity are not straight but convex towards the abscissa. The present investigation reveals that this is invariably the case for all rare gas mixtures. In the semi-logarithmic scale, however, very nearly straight lines have been obtained. This means that the thermal conductivity of a binary mixture of rare gases is, to a first approximation, the geometric mean of the conductivities of the pure constituents, i.e.:

$$K_{12} \approx K_1^a \cdot K_2^b,$$

where a and b are the atom concentration of the two constituents.

Departures from this rule occur, however, particularly as the difference in atomic weight becomes larger. It is therefore most pronounced for the He-Xe mixtures: the curves on the semi-log scale are somewhat concave towards the abscissa, but near the He-end a convexity may be observed.

For the sake of comparison the writer has replotted on a semilogarithmic scale (not reproduced here) an elder A-He series (Wachsmuth, 1908) and the

Table 2. Thermal conductivities of the ternary mixtures Xe-Kr-He (in units of 10^{-7} cal/cm² degree sec).

(Xe-Kr mixtures containing basically the percentage of Kr listed at the left end of the table have been diluted with He)

	% He	29°C	520°C	s
11 % Kr	0	145	338	0.88
	21.9	405	860	0.78
	48.6	916	1990	0.80
	70.9	1580	3450	0.81
	86.4	2470	5080	0.75
15.8 % Kr	0	149	341	0.86
	24.8	455	976	0.79
	48	893	1880	0.77
	74.2	1710	3620	0.78
	86.5	2390	4880	0.74
27.6 % Kr	0	158	358	0.85
	21.5	412	958	0.79
	50.7	964	2030	0.77
	70.6	1520	3390	0.83
	85.9	2380	4830	0.73
51 % Kr	0	186	420	0.85
	22.7	450	995	0.82
	47.9	928	1950	0.79
	72.9	1740	3780	0.81
	85.6	2300	5340	0.87
78.5 % Kr	0	206	479	0.87
	24.5	533	1140	0.79
	51.9	1060	2250	0.78
	74.3	1840	3840	0.76
	86.5	2500	5120	0.74

recent measurements of Srivastava and Saxena (1957) on Ne-A, Ne-Kr and A-Kr. With the exception of the A-Kr series, where values lay about 6 % lower, they confirm the present results. As far as ternary mixtures of He-Kr-Xe are concerned, it is interesting to note that they behave as if a gas with properties intermediate to those of Kr and Xe has been mixed up with He.

Work on the theoretical evaluation of these results is in progress.

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